ANALYSIS OF GAS SAMPLES FROM COALBED METHANE WELLS IN SULLIVAN COUNTY, INDIANA USING GAS CHROMATOGRAPHY

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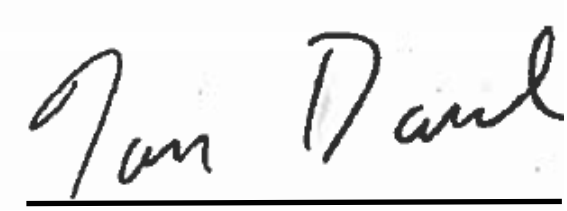

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Table of Contents

Abstract

Although there has been an increase in natural gas production from coalbed methane (CBM) reservoirs in the past few decades, there are multiple inadequately known aspects of CBM reserves. To understand the systematics of CBM production, twenty gas samples were collected from producing coalbed methane wells in Sullivan County, Indiana. These wells are producing from the Springfield and Seelyville coal seam units in the Illinois Basin and have been characterized for their noble gas chemistry previously. Here, the hydrocarbon molecular composition, isotopic composition of carbon and hydrogen in methane, and major gas composition (N_2, CO_2) are reported. One of the goals of this experiment is to use the composition of produced gases to determine the relative proportions of major inert gases compared to economically viable hydrocarbon gases. Another goal of this thesis is to use the composition of the produced gases to determine if natural gas formation in coal seams in the Illinois Basin is formed by biogenic processes or thermogenic processes. Based on the analyses conducted in this experiment, it appears that the wells have a dry gas composition (<1% ethane plus) and contain 2.7 to 10.6% non-hydrocarbon gases (N_2, CO_2). Based on the presence of ethane in the majority of wells, one can conclude that there is a mixture of biogenic and thermogenic natural gas forming in the Springfield and Seelyville coal seams.

Key Words: coalbed methane, Illinois Basin, hydrocarbon molecular composition, isotopic composition of methane

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Introduction

The ever-growing need to reduce carbon emissions has driven scientific and industry research away from coal toward the extraction of lower polluting, unconventional energy resources such as coalbed methane (CBM) and other sources of natural gas (Kerr, 2010; Darrah et al. 2014). The relatively recent dependence on unconventional resources has produced many questions about the genetic source (biogenic vs. thermogenic), migration (in situ versus trapped), and evolution (e.g., degradation by microbes or other oxidizing reactions) of these natural gas deposits (Burruss and Laughrey, 2010; Tilley and Muehlenbachs, 2012; Hunt et al., 2012; Darrah et al., 2014; Darrah and Poreda, 2012). To address these issues, I examined the molecular and isotopic composition of natural gas samples from the Illinois Basin. The samples used in this study were acquired from Sullivan County, Indiana because it is an ideal location for coalbed methane (CBM) production (Figures 1 and 2).

This study area is in close vicinity to the first economically viable CBM project in the Illinois Basin and sits between multiple active CBM/New Albany Shale projects. The coal fields accessed for CBM production in this area are near the center of the largest surface coal mine east of the Mississippi River and is also just east of the highest gas content coal measured in the Illinois Basin (Buschbach and Kolata, 1990).

The Illinois Basin is an oval-shaped syncline spanning about 1.55 $x10^4$ square kilometers and extending from central Illinois to western Indiana and northwestern Kentucky (Buschbach and Kolata, 1990). It is bounded by the Mississippi River Arch to the northwest, the Kankakee Arch to the northeast, the Ozark dome to the southwest, and the New Madrid Rift Complex to the south (Buschbach and Kolata, 1990). The structural and hydrographic features separate the

Illinois Basin from adjacent basins such as the Appalachian Basin (to the east), the Forest City Basin (to the west), and the Michigan Basin (to the northeast) (Buschbach and Kolata, 1990).

The Illinois Basin is an intracratonic basin that that formed during Appalachian tectonics spanning from approximately 530 to 280 million years ago (Strąpoć et al., 2007). Sedimentation in the Illinois Basin occurred during transgressive phases and led to infills up to 3.7 $x10^3$ meters thick near the basin center, which largely consisted of shallow to deep marine sediments (Strąpoć et al., 2007). During the Devonian, sedimentation occurred within a semi-restricted basin that produced a stratified, anoxic, marine environment that led to the burial of organic-rich sediments (Cluff, 1980), which eventually lead to the formation of the New Albany Shale. The New Albany Shale is the dominant oil- and gas-producing unit in the Illinois Basin (Strapoc et al., 2010). Currently, depths to the New Albany Shale range from surface outcrop at the edges of the Illinois Basin to near 1.5 $x10^3$ meters at the basin center. Thermal maturities of the New Albany Shale range from approximately 0.54% vitrinite reflectance (R_o) on the margins of the basin to 1.5% (R_o) near the center of the basin (Cluff, 1980; Strapoc et al., 2010).

The Pennsylvanian-aged coal-bearing strata in the Illinois Basin were deposited from ~318 to 299 million years ago and are divided into three major units: the McLeansboro, the Carbondale, and the Raccoon Creek Groups (Strąpoć et al., 2007). Deformation of the Illinios Basin that formed the macroscopic syncline characterizing the Illinois Basin produced stress on the coal bed seams, inducing fractures, layer parallel shortening, low amplitude folding, and cleating. This deformation allowed cleats to expand in size, which allowed natural gas to be

released and fresh water to flow in, especially following periods of glaciation (Cluff, 1980; Schlegel et al., 2011; Strapoc et al., 2010).

Gas samples included in this study were collected from producing coal bed methane wells that are sourced from the Springfield coal seam of the Petersburg Formation and the Seelyville coal seam of the Linton Formation (purple boxes Figures 1 and 2, Table 1). The Springfield coal seam ranges in thicknesses of 1.37–1.83 meters and outcrops at the surface and can get as deep as 260m. The Seelyville ranges in thicknesses of 0.3-3 meters and ranges in depths from surface to 277 m. deep at the depocenter (Drobniak et al., 2004).

Goals and Objectives

Natural gas consists of a mixture of different gases including hydrocarbon gases (CH_4, C_2H_6, C_3H_8, C_4H_{10}, etc.), major gases (N_2, CO_2, O_2, etc.), noble gases (He, Ne, Ar, etc.) and sulfides (H_2S, COS, etc.) (Akansu et al., 2004; Darrah et al., 2015; Darrah and Poreda, 2012; Moore, 2012). Determination of gas quality or composition demands that one examines the types of gases inherently present in each producing well, or reservoirs more broadly. There are productive gases and inert gases. Productive hydrocarbon gases (methane, ethane, propane, etc.) are those that add economic value, typically determined by heat content (i.e., BTU or British Thermal Unit) content, and inert gases (CO_2, N_2) which do not combust and thus take away value (Akansu et al., 2004; Moore, 2012).

The overall goals of this research were to analyze the gas samples acquired from producing coalbed methane wells in Sullivan County, Indiana, to determine the hydrocarbon and non-hydrocarbon molecular content and the isotopic composition of carbon and hydrogen in methane. Previous work by our laboratory group has characterized the noble gas composition (Moore, 2016). To be more specific, the following research was conducted to:

1. Evaluate the quality of natural gas produced from unconventional coal seams in Sullivan County, Illinois (more specifically the Seelyville and Springfield coal seams) to determine its viability for future coalbed methane production. To do this, one must determine how much of the producing natural gas is made up of economically viable hydrocarbon gases (e.g., methane, ethane, propane, butane, pentane), compared to how much is made up of inert (noble gases) and non-hydrocarbon gases (e.g., N_2, CO_2) that can reduce profit and or lead to contamination (e.g., H_2S is toxic, can be fatal, and is also very corrosive to casing and pipelines) (Moore, 2012).

2. Identify whether the coalbed methane gas sources are characterized as “dry” or “wet” gas. Dry natural gas is made up of a much greater proportion of methane compared to other gases. This study uses 95% as the cut-off between a “dry” gas and wet gas (<95% methane). This study will quantify how many of the wells in Sullivan County, Indiana are producing dry natural gas vs. wet natural gas based on methane content. I also compared the hydrocarbon molecular content (C_1/C_2+) to see how methane compares with higher-ordered aliphatic hydrocarbon chains in wells that produce dry vs. wet natural gas.

3. To determine if natural gas being produced from the Springfield and Seelyville coal seams is biogenic, thermogenic, or a mixture of biogenic and thermogenic origins. Methanogens can consume organic matter adhered to coals and produce biogenic methane by the reduction of CO_2 or acetate fermentation (Ritter et al., 2015; Schoell, 1988). In contrast, thermogenic methane forms from the thermocatalytic decomposition of kerogen with increasing pressures, temperatures and burial depths (Tilley and Muehlenbachs, 2006). Based on the stratigraphy, the Springfield and Seelyville coal seams could be acting as stratigraphic traps for deeper migrated thermogenic gases. The two processes to form biogenic and thermogenic natural gas could be taking place in tandem to form a mixture of biogenic and thermogenic natural gas (McIntosh et al., 2002; Schlegel et al., 2011). One can compare the hydrocarbon molecular content (C_1/C_2+) against the isotopic composition of carbon in methane ($\delta^{13}C\text{-}CH_4$) (Bernard et al., 1978; Whiticar et al., 1985) and the isotopic composition of hydrogen in methane ($\delta\,^2H\text{-}CH_4$) against $\delta\,^{13}C\text{-}CH_4$ (Schoell, 1980; Schoell, 1988) to determine if the natural gases in the Springfield and Seelyville coal seams are biogenic, thermogenic, or a mixture of biogenic and thermogenic gases.

Methods

Sample Selection and Collection:

I measured 20 gas samples collected from actively producing CBM wells for hydrocarbon geochemistry (molecular; C_1/C_2+ and stable isotopic composition of carbon and hydrogen in methane (i.e., $\delta^{13}C\text{-}CH_4$ and $\delta\ ^2H\text{-}CH_4$) and major gas composition (N_2, CO_2) in Sullivan County, Indiana. Five wells were producing from the Springfield coal seam from CBM wells at screened intervals of 76 to 210 meters depth (Tables 1; 2; and 3). The data from these wells are denoted as red diamonds in Figures 5–8. Nine wells were producing from the Seelyville coal seam from CBM wells at screened intervals of 150 to 210 meters below land surface (Tables 1; 2; and 3). The data from these wells are denoted as red circles in Figures 5–8. Six wells were sampled that are screened in the Springfield and Seelyville coal seams, these are denoted as "comingled production" (Tables 1 and 3) and data from these gases are shown by a red triangle in Figures 5–8.

Gas samples were collected from actively producing CBM wells using 0.95 cm. diameter and 40.6 cm. long refrigeration-grade copper tubes. Copper tubes were connected in-line of the CBM well and after flowing production gas for approximately fifteen minutes (>50 copper tube volumes) through the copper tubes, gas samples were sealed within the copper tube using brass clamps.

Sample Preparation and Analysis:

In the laboratory, the gas samples in the copper tubes were prepared for analysis by re-clamping approximately 2.5 cm splits of the copper tubing using stainless steel clamps. Next, the copper tube was attached to an ultra-high vacuum steel line (total pressure= 1-3 $x10^{-9}$ torr),

which is monitored continuously using a four digit (accurate to the nearest thousandths) 0–20 torr MKS capacitance monometer, using a 0.95 cm. Swagelok ferruled connection. After the sample connection had been sufficiently evacuated and pressure was verified, an aliquot of the gas sample was introduced into the ultra-high vacuum line by re-rounding the copper for major gas composition measurements using a SRS-RGA quadrupole mass spectrometer and SRI Model 8610C SRI GC. This process was repeated sequentially on vacuum introduction lines for the gas chromatograph for each of the 20 samples.

Hydrocarbon and non-hydrocarbon gases were analyzed using an SRI Model 8610C Multiple Gas Chromatograph #3. The Multiple Gas #3 is a type of Gas Chromatograph that separates chemical substances and is designed to measure many gases, such as CO, CO_2, CH_4, C_2H_6, C_3H_8, C_4H_{10}, and C_5H_{12} in a single analysis of a sample. After injection of a gas sample, the instrument generates a series of responses measured in millivolts (mV) on the x-axis against time on the y-axis. That series of peaks (the visual in the graph for the responses) is known as a chromatogram. Each peak in the chromatogram represents a specific compound that is present and the concentration of that compound in the gas sample is determined by comparison to known standards. The separation of each compound is determined by two limits on the chromatogram; retention time, which is the time from the point of injection to the peak maximum, and peak area, which represents the amount of sample present.

The Multiple Gas #3 GC uses a software program called “PeakSimple” to organize hardware events and temperature control to test for different compounds using the GC (the hardware and temperature controls for this study are displayed in Figures 4A and 4B). The events table is set-up prior to the gas sample being analyzed, it is time-based and the user can

decide when to open and close each valve to release the gas sample into the detector (Figure 4A). As one can see the "G valve" in the hardware event only needs 0.2 seconds for enough sample to enter to the column and then later on the detector for the analysis to be complete (Moore, 2016). The temperature control software is also time-based, the user can input at what rate the gas sample is heated up and for how long the GC will remain heating the gas sample at that temperature (Figure 4B). It should be noted in this study that the GC held a temperature of 250^{o}C for 15 minutes to ensure that even heavier hydrocarbons like pentane, iso-pentane, and hexane could be measured. Peaks representing different compounds on a chromatogram typically will display themselves in increasing molecular weight with increasing time (with iso-butane peak appearing slightly earlier than butane, iso-pentane peak appearing slightly earlier than pentane and so forth for hexane). For example, when heating up a sample that contained C_1–C_6 (shorthand for methane to hexane) hydrocarbons, the first peak would be methane because it is the lightest gas and would volatize/separate first from the sample, the following peak would be carbon dioxide because it is the next lightest gas, and would volatize/separate second from the gas sample.

The SRI Model 8610C Multiple Gas Chromatograph #3 uses helium as its carrier gas and is equipped with three detectors. Each detector within the GC is used to detect different gases. The Flame Photometric Detector (FPD) is used to measure sulfur bearing compounds, such as H_2S or SO_2. The Thermal Conductivity Detector (TCD) measures the difference in thermal conductivity in the carrier gas and the sample gas. It is less sensitive than the other detectors, however it can show all molecules with boiling points below hexane, including; CO_2, Methane, Oxygen, CO, Hydrogen, Nitrogen, Water, and most importantly Hydrocarbons. The TCD will

measure all non-sulfur molecules and has a detection range of approximately 0.1% to 100% (100-1,000,000ppm) (Moore and Whyte, 2015).

Though this GC is equipped with three detectors the detector used in this study is the Flame Ionization Detector (FID) Methanizer. Hydrogen gas flows through the GC to ensure that the flame can remain lit. This detector can show a response to any carbon-bearing compound. The detector does not register a peak for sulfur-containing compounds nor nitrogen and oxygen. With a detection range from 0.1ppm to almost 100% (Moore and Whyte, 2015) this is the most sensitive detector for hydrocarbons and therefore this detector is used to determine the hydrocarbon molecular content (C_1/C_2+) (Moore and Whyte, 2015).

Methods to analyze gas samples on the MultiGas #3 GC:

Gas samples are stored in an air-tight copper tubing.

Tubing is inserted onto vacuum line to syringe 10–20 mL of sample into plastic syringe.

Syringe is cleared with room air in between samples, as is the vacuum line that was used to collect sample.

Inject 10–20mL of sample into GC inlet.

*Note-1ml of sample is actually analyzed (the rest clears the line)

Gas flows through channels 1 and 2 detectors.

A Haysep-D column (1.83 meters in length) will then separate out the heavier gases, such as; ethane- hexane, CO_2, but not O_2 and N_2, which will show a big peak.

Gas will flow through the T.C.D, peaks are not as large as F.I.D, but will be registered earlier on the graph. T.C.D can detect O_2, H_2, N_2, and all molecules with weights less than hexane.

Gas flows through F.I.D and peaks will register later but larger because the F.I.D is more sensitive, and the F.I.D will recognize hydrocarbons that weigh less than hexane.

Chromatogram will form in the Peaksimple software. The user must identify which peaks are which compounds and the area of the peak to determine what concentration of gas sample is present.

The integration tool in Peaksimple software may have to be used to make sure the software system is identifying peaks correctly and registering the correct areas for the correct compounds.

Notes to remember:

1) When a buzz noise is present, and there is a spike on the chromatograph valve G + A on/off because the Gaussian peaks are molecules and the quiet spikes are valves that are changing.
2) T.C.D. Protect: The light turns on when there is no carrier gas present.

For all major and hydrocarbon gas concentrations, the standard analytical errors were all less than ±3.36% for concentrations above detection limits. Average external position for hydrocarbon and major gases were determined by "known-unknown" standard experimentation using an atmospheric air standard (Columbus, Ohio air) and synthetic standards obtained from the company Praxair. The errors of this analysis are as follows: CH_4 (2.19%), C_2H_6 (2.78%), N_2 (1.25%), CO_2 (1.06%), H_2 (3.41%), and O_2 (1.39%) based on daily replicate measurements.

The values for $\delta^{13}C\text{-}CH_4$ and $\delta^{2}H\text{-}CH_4$ were measured at Isotech Laboratories (Champaign, Illinois). The procedures for isotopic analysis of carbon and hydrogen in methane at Isotech were summarized previously (Darrah et al., 2015; Darrah et al., 2014; Jackson et al., 2013; Osborn et al., 2011). The isotopic signatures of hydrogen in methane are denoted in per mil versus Vienna standard means ocean water (VSMOW) with an approximate standard deviation of ± 0.5 ‰ (Gonfiantini et al., 1995). The isotopic signatures of carbon in methane are expressed in per mil versus Vienna Peedee belemnite (VDPD), with a standard deviation of ± 0.2 ‰ (Gonfiantini et al., 1995). Using chromatographic separation followed by combustion and dual-inlet isotope ratio mass spectrometry, the detection limits for $\delta^{13}C\text{-}CH_4$ and $\delta^{2}H\text{-}CH_4$ were 0.001 and 0.001 (Isotech laboratories, 2012). The methods used in this laboratory followed previously used methods (Darrah et al., 2013; Darrah et al., 2014; Darrah et al., 2015).

Results

Data were collected in this study from 20 CBM wells producing from the Springfield coal seam, the Seelyville coal seam, and from co-mingled production from both coal seams. For the interpretation of these results, I treat all 20 samples as one group and recognize that this limits the interpretations that can be made from this study.

CH_4 concentrations ranged from 0.875 to 0.973 ccSTP/cc with 0.944 ccSTP/cc on average. C_2H_6 concentrations ranged from 7.1 x 10^{-5} to 1.1 x 10^{-3} ccSTP/cc with 3.6 x 10^{-4} ccSTP/cc on average (Tables 1 and 2). The N_2 concentrations ranged from 0.020 to 0.097 ccSTP/cc with 0.045 ccSTP/cc on average. The CO_2 concentrations ranged from 0.004 to 0.017 ccSTP/cc with 0.009 ccSTP/cc on average (Tables 1 and 2). The concentrations of C_3H_8, C_4H_{10}n, C_4H_{10}i, C_5H_{12}n, C_5H_{12}n, and C_5H_{12}i (where i denotes iso, meaning C_4H_{10}i is isobutane and the n denotes normal, meaning C_4H_{10}n would be butane) were all below the detection limit of 1 x 10^{-5} ccSTP/cc (Tables 1 and 2).

The δ^{13}C-CH_4 values ranged from -69.80‰ to -49.87‰ with -58.39 ‰ on average. The δ^{2}H-CH_4 ranged from -214.9‰ to -201.4‰ with an average of -207.1‰. The CH_4/C_2H_6+ (denoted as C_1/C_2+ in the plots) ratios ranged from 867.6 to 13256.6 with 4348.5 on average (Tables 3 and 4).

Discussion

The overall goals of this research were to: 1) evaluate the quality of natural gas produced from unconventional coal seams in Sullivan County, Illinois; 2) identify whether the coalbed methane gas sources are characterized as "dry" or "wet" gas; and 3) to determine if natural gas being produced from the Springfield and Seelyville coal seams are biogenic, thermogenic, or a mixture of biogenic and thermogenic origins.

Goal 1: Quality of the Natural Gas

Because the summed concentrations of N_2, CO_2, He, and Ar account for >99.95% of all non-hydrocarbon gases, we use these components as metric for the quality of natural gas. With these parameters, the proportion of non-hydrocarbon gases within the CBM produced gases from this study area range from 2.7% to 10.6% (Table 1). The samples suggest a range in BTU content from 817.1 to 923.1 BTU for bulk gas. While it is cost prohibitive to remove N_2, He, Ar or other inert gases, CO_2 can be easily removed by cryogenic cycling (USEIA, 2014). Thus, we also report the BTU content after CO_2 removal. After CO_2 removal, the BTU values increase by 8.6% on average and range from 907.1 to 926.3.

The main factor that seems to control the proportion of hydrocarbon and non-hydrocarbon gases is the relative proportion of natural gas and water-derived gases in the sample. When methane concentrations increase, there is a strong negative correlation (r^2= -0.98) of decreasing air-saturated water components, shown by relative to [N_2] (Figure 5A). This results from the fact that methane and N_2 (sourced from nitrogen dissolved in groundwater) are the two dominant gases in all producing natural gas wells. In general, a similar result relative to methane is observed for argon (Ar).

This same observation does not hold true when comparing [CH_4] with [CO_2] or He (shown as CO_2 in Figure 5B). The lack of correlations between CH_4 and either CO_2 or He can likely be attributed to variable roles of microbial activity on CO_2, including methanogenic consumption of CO_2 to generate methane and methanotrophic oxidation of organic matter and natural gas to CO_2 (Darrah et al., 2015). In addition, carbon dioxide is highly soluble in water, and thus can be affected by variable gas-water ratios. Consistent with CO_2, He appears to be more variable and can result from a collection of thermogenic contributions, variations in groundwater age, and relatively high microbial consumption of natural gas to CO_2. As I will discuss later, the preponderance of data suggests that elevated helium levels are dominated by the introduction of thermogenic methane.

Goal 2: Dry or Wet Natural Gas

In addition to non-hydrocarbon gases, the composition of hydrocarbons is essential to evaluating the quality of natural gas samples. While dry gas (dominantly methane) is exceptionally clean burning and highly energy efficient, wet gas has a higher BTU content, is more easily transported as a liquid, and as such is more valuable for most commercial operations (Whiticar et al., 1985). As a result, wet gas is commonly a target for economic hydrocarbon recovery. For these reasons, wetness (defined as C_2+/C_1 x 100%) is critical to evaluating the economic potential of unconventional gas fields.

The range of C_1/C_2+ from 867.6 to 13,256.6 suggests that all samples collected as part of this study would be classified as dry gas because the proportion of C_2+/C_1 x100% (in the hydrocarbon gas phase only) is significantly less than 5% for all samples (Table 1). While all of these samples do contain quantifiable ethane levels (but almost no detectable propane or higher

order compounds) and significantly lower C_1/C_2+ than anticipated for a purely microbial end-member (discussed further below), these gases are all dry gas. Thus, although this field would represent a clean emitting, and potentially renewable fuel choice, it has relatively low BTU content compared to other unconventional natural gas fields such as the Marcellus and Utica (Darrah et al., 2014; Darrah et al., 2015; Burruss and Laughrey, 2010).

Goal 3: Biogenic, Thermogenic or Both?

The classic method to distinguish biogenic and thermogenic natural gases compares plots of C_1/C_2+ vs. $\delta^{13}C\text{-}CH_4$ (referred to as "Bernard Plots"; Figure 7) (Bernard et al., 1978; Claypool et al., 1980; Rice and Claypool, 1981) or plots of $\delta^{2}H\text{-}CH_4$ vs. $\delta^{13}C\text{-}CH_4$ (referred to as "Schoell Plots" or "Whiticar Plots"; Figure 8) (Schoell, 1980; Schoell, 1988; Whiticar et al., 1985). In these plots, natural gases that have a biogenic origin show highly elevated ratios of C_1/C_2+ >>~2000 and $\delta^{13}C\text{-}CH_4$ <~-60 to 65‰, whereas thermogenic gases will have ratios of C_1/C_2+ = 0.25 to 60 and $\delta^{13}C\text{-}CH_4$ >~-50‰ (typically >-45‰) (shown in Figures 7 and 8). Since methanogens cannot produce ethane (Jackson et al., 2013), increasing ethane concentrations can be indicative of thermogenic contributions to the Springfield and Seelyville coal seams.

When comparing the C_1/C_2+ against the $\delta^{13}C\text{-}CH_4$, the majority of samples would be classified as either "microbial" or near microbial along a mixing trend toward the "thermogenic gas" composition (Figure 7). The presence of small amount of ethane can be indicative of a relatively small proportion of thermogenic gas mixing with dominantly biogenic gases. This is seen in Figure 6A, where there is a weak association of ethane concentrations increasing with increasing methane concentrations (elevated methane can be thought of as higher proportion of natural gas with respect to groundwater contributions). As stated earlier, thermogenic natural gases tend to form more isotopically heavy (more enriched in heavier isotopes) carbon and

hydrogen signatures in methane. It seems that more thermogenic in origin natural gases could be contributing to the Springfield and Seelyville coal seams, because we see relationship between heavier carbon in methane isotopes with higher methane concentrations (figure 6C).

Schoell has demonstrated that $\delta^2H\text{-}CH_4$ can be used to differentiate between near-surface microbial methane (lighter $\delta^2H\text{-}CH_4$ -350‰ to -270‰) that is associated with acetate fermentation from sub-surface microbial methane (heavier $\delta^2H\text{-}CH_4$ -250‰ to -170‰) that is associated with carbon dioxide reduction (Figure 8) (Schoell, 1980). When comparing $\delta^2H\text{-}CH_4$ against $\delta^{13}C\text{-}CH_4$ of gas samples from producing CBM wells in Sullivan County, Indiana one can notice that some samples fall in the "sub-surface microbial" zone, but a majority fall along a mixing line between sub-surface microbial gases and the "thermogenic methane" zone (Figure 8). As stated in the literature review, sub-surface microbes will be using CO_2 reduction to form methane. Therefore, based on Figure 8, it appears that a mixture exists of biogenic natural gas being formed from CO_2 reduction and deeper thermogenic natural gas migrating into the Springfield and Seelyville coals seams in tandem. Based on the available data, we conclude that the majority of gases produced from CBM reservoirs in this area is dry gas. These gases likely result from the combination of biogenic and thermogenic end-members, possibly in shallow water-dominated coal seams.

Conclusions

During this study, I collected 20 gas samples from CBM wells producing from the Springfield and Seelyville coal seams in Sullivan County, Indiana and analyzed them for hydrocarbon molecular content, isotopic composition of carbon and hydrogen in methane and major gas composition. This study determined that these wells produce 2.7 to 10.6% inert gases using the combined concentration of CO_2 and N_2 as the proxy for "inert gases." I also found from conducting these analyses that all producing CBM wells yielded a dry natural gas composition ($\geq$95% [CH_4]).

By plotting C_1/C_2+ against $\delta^{13}C\text{-}CH_4$ and $\delta^{2}H\text{-}CH_4$ against $\delta^{13}C\text{-}CH_4$, we have shown that there is a mixture of biogenic and thermogenic natural gas present in the Springfield and Seelyville coal seams. By using the Schoell plot, we can demonstrate that the biogenic in origin natural gas is forming from CO_2 reduction. Based on the data it appears that biogenic in origin natural gas is being formed in-situ of the Springfield and Seelyville coal seams, while there also appears to be thermogenic natural gases mixing into the Springfield and Seelyville coal seams in tandem.

Recommendations for Future Work

This study helped to explain the gas composition from producing CBM wells in the Illinois Basin. However, there is still much work that can be done in this region. First, more sampling can be done within the Illinois Basin. A more robust data set from different time periods can help us to determine if the inert gas production that we see changes with seasons or with more natural gas production. This time-series analysis can also be applied to the amount of [CH_4] observed in producing wells, to see if they are changing over time as production increases in the region. I would like to apply the methods I used in this study to see the composition of natural gases in wells that produce natural gas from shale plays, etc. and even in other CBM basins.

Figures

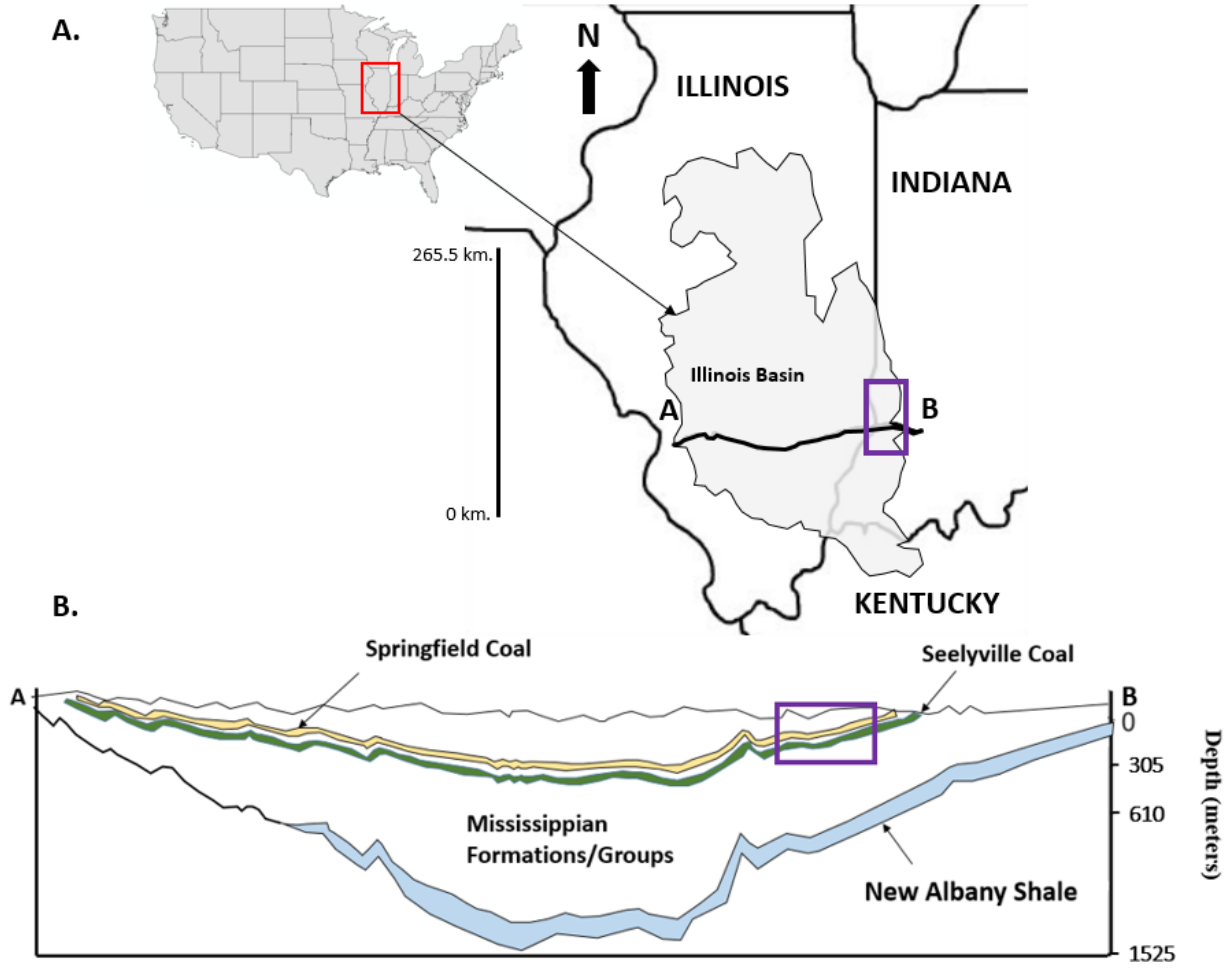


Figure 1: Areal extent of the Illinois Basin (B) and a simplified structural cross section of the synclinal Illinois Basin (C) reproduced from (Moore, 2016; Strąpoć et al., 2007). Samples were collected from producing coalbed methane (CBM) wells in the area denoted by the purple box along the eastern portion of the Illinois Basin.

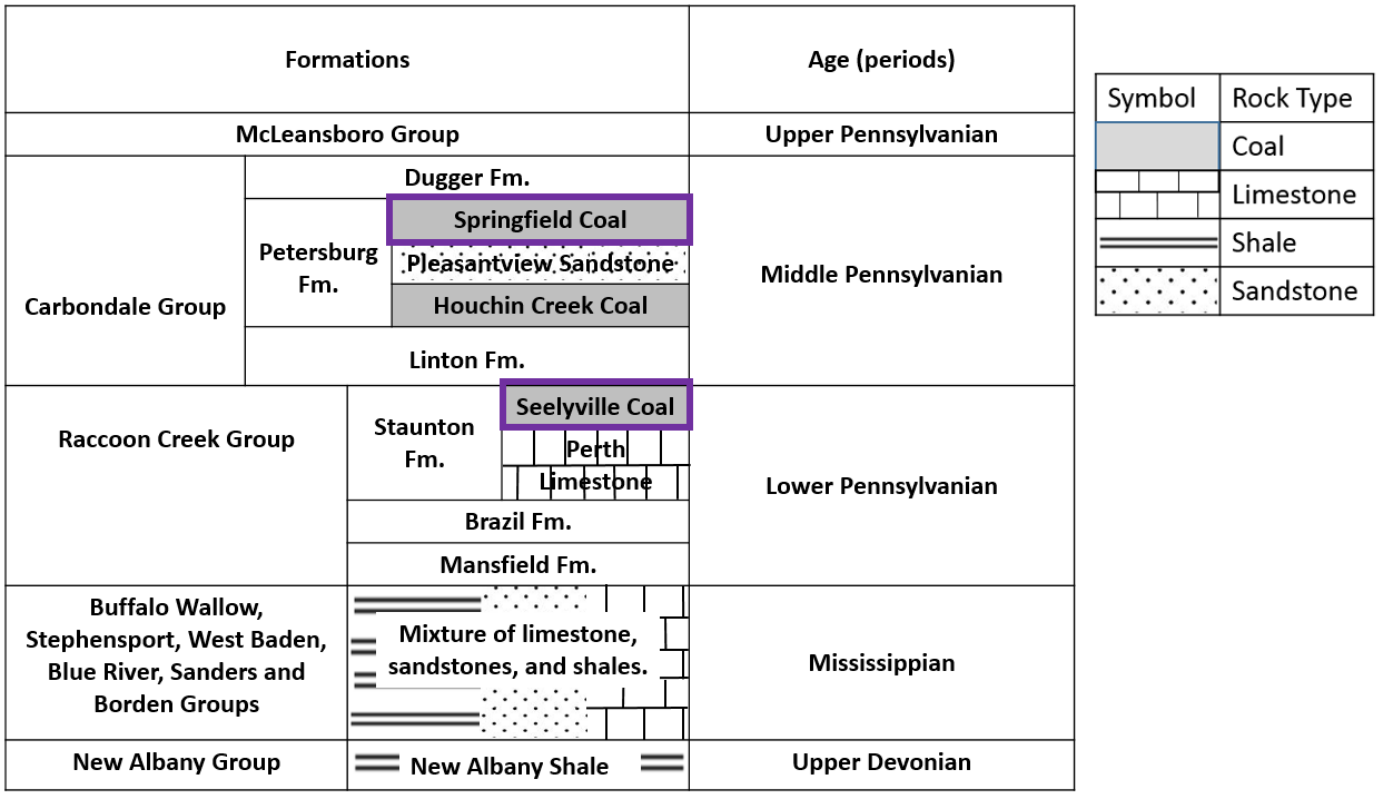


Figure 2: Generalized stratigraphic column (reproduced from Moore, 2016) of the Illinois Basin in Sullivan County, Indiana. CBM wells sampled in this study were producing from the Springfield and Seelyville coal seams (denoted in purple boxes in this column).

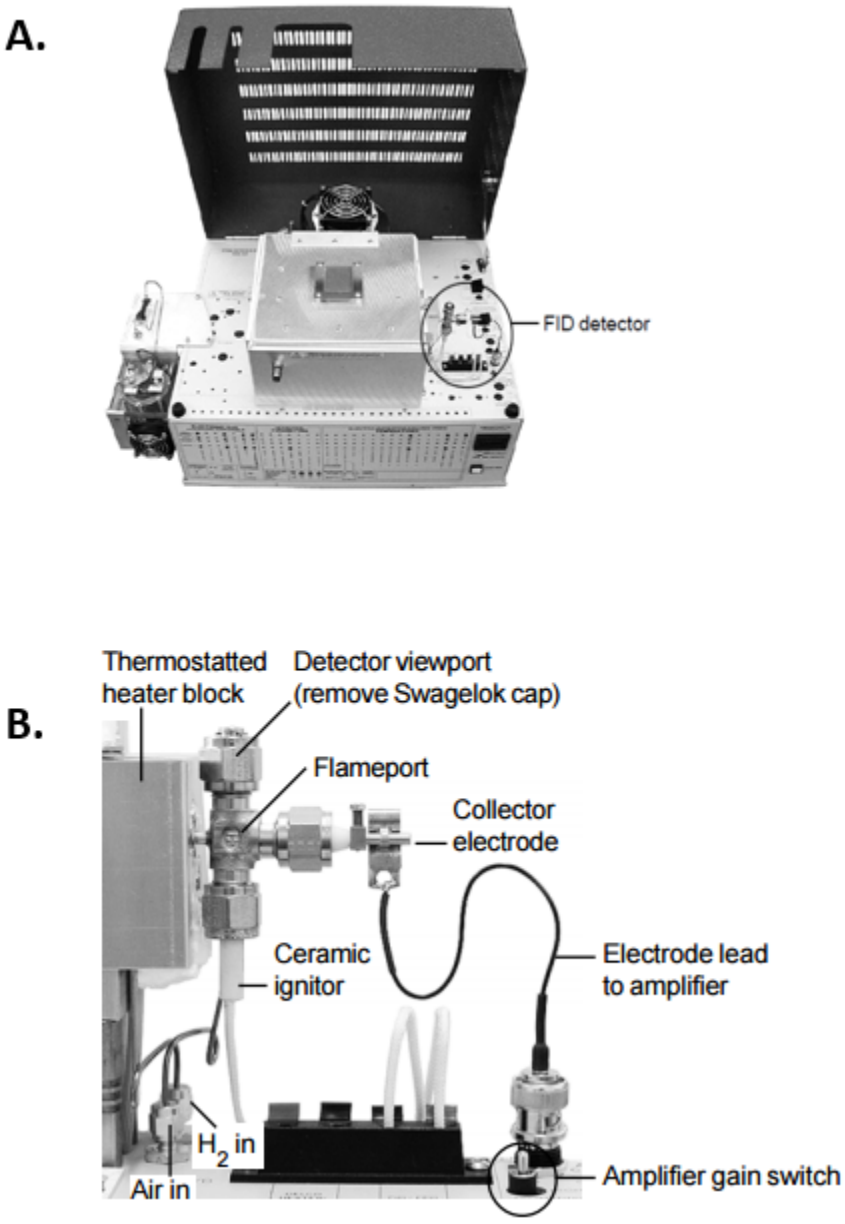
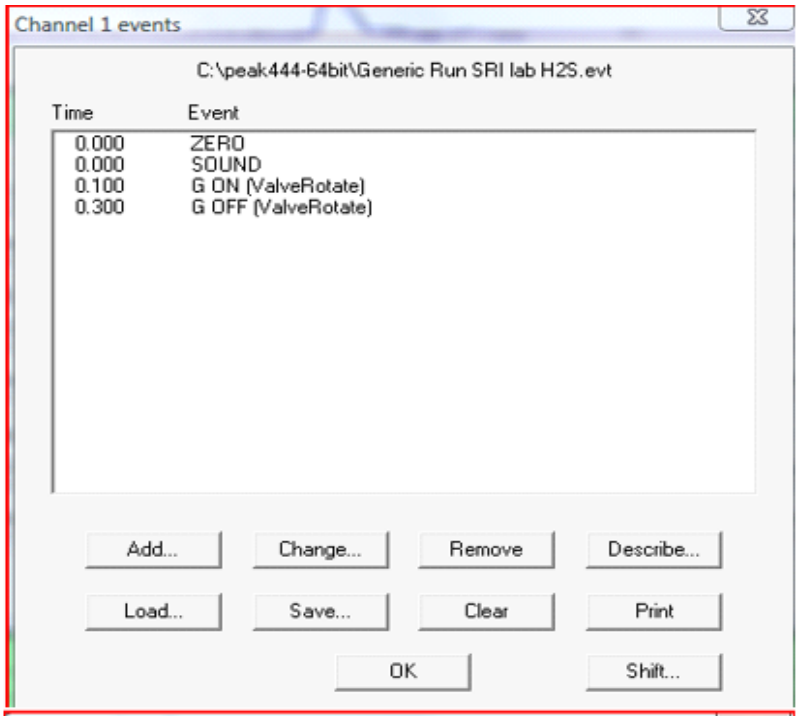


Figure 3: Photograph of the SRI-8610C multi-gas chromatograph equipped with a flame ionization detector (A) and a zoomed-in view showing the different parts of the detector (B) (SRI Instruments 2012).

A.



B.

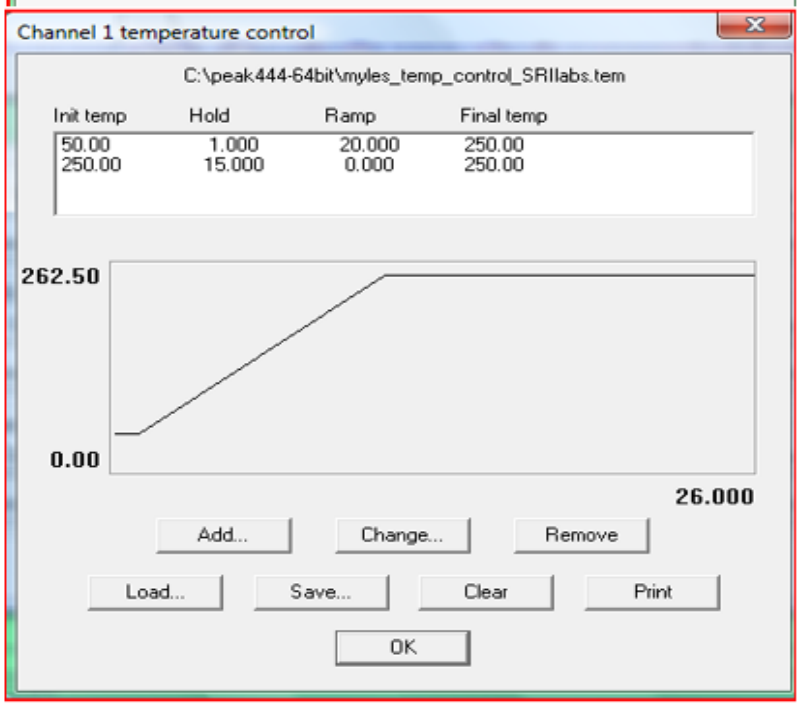


Figure 4: Hardware events (A) and temperature controls (B) using PeakSimple software.

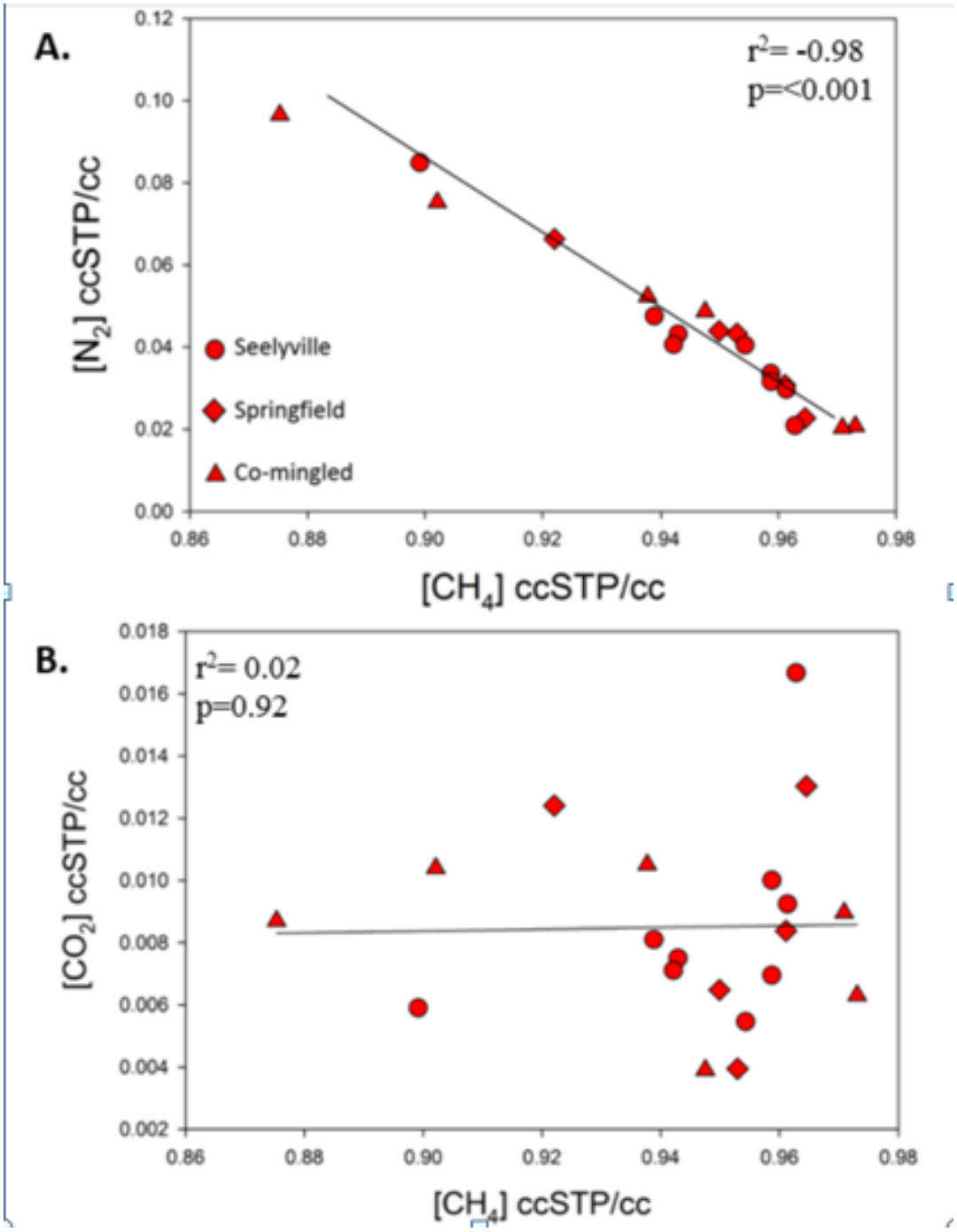


Figure 5: [N_2] (A) and [CO_2] (B) concentrations plotted against [CH_4] concentrations of 20 producing CBM wells from the Illinois Basin. Units that the wells were producing from are denoted in red symbols.

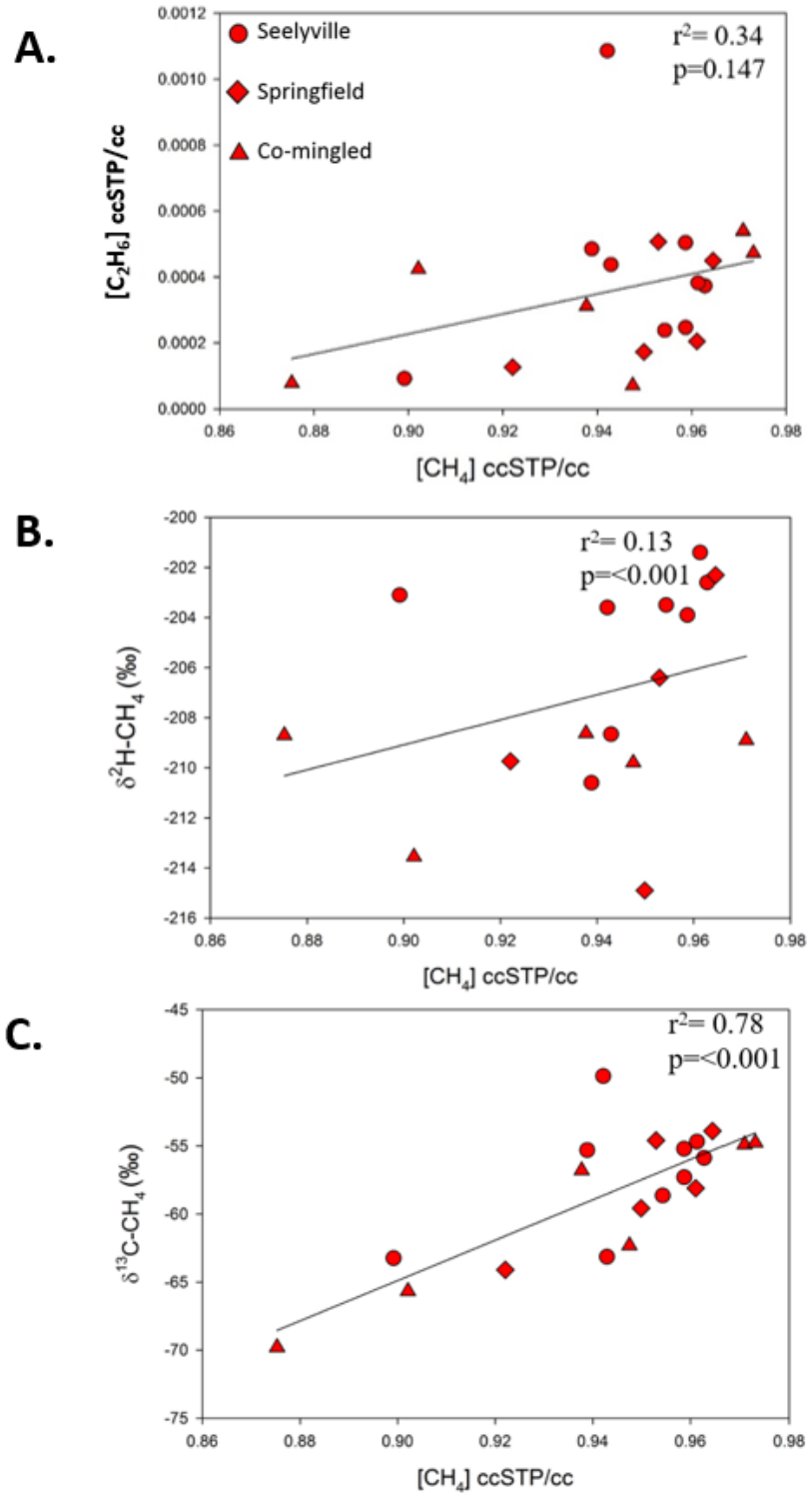


Figure 6: [C_2H_6] (A), δ^2H-CH_4 (B), and δ^{13}C-CH_4 (C) plotted against [CH_4]. Only 17 of the 20 samples had enough hydrogen concentration to determine δ^2H-CH_4.

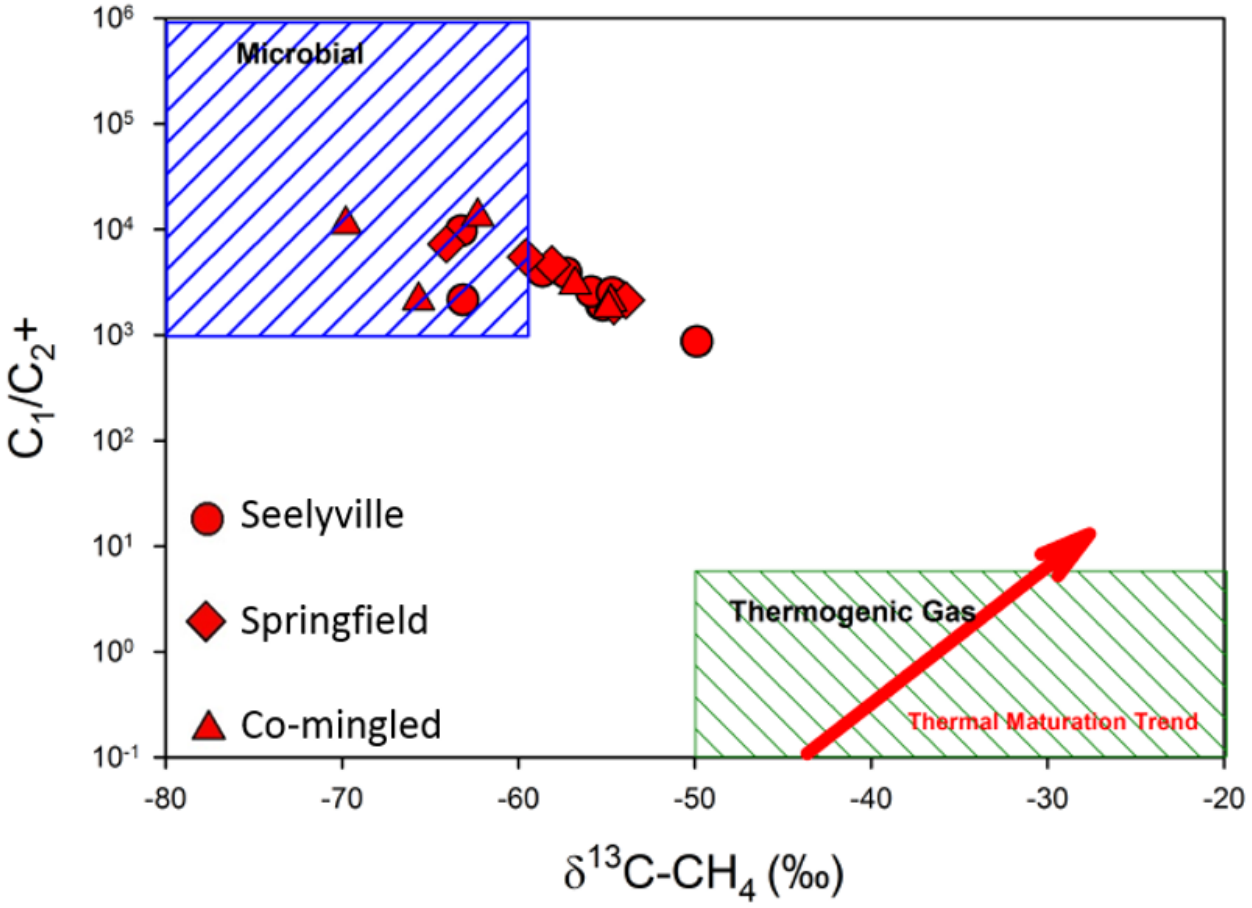


Figure 7: Ratio of methane over higher-ordered aliphatic hydrocarbon chains (C_1/C_2+) vs. $\delta^{13}C\text{-}CH_4$.

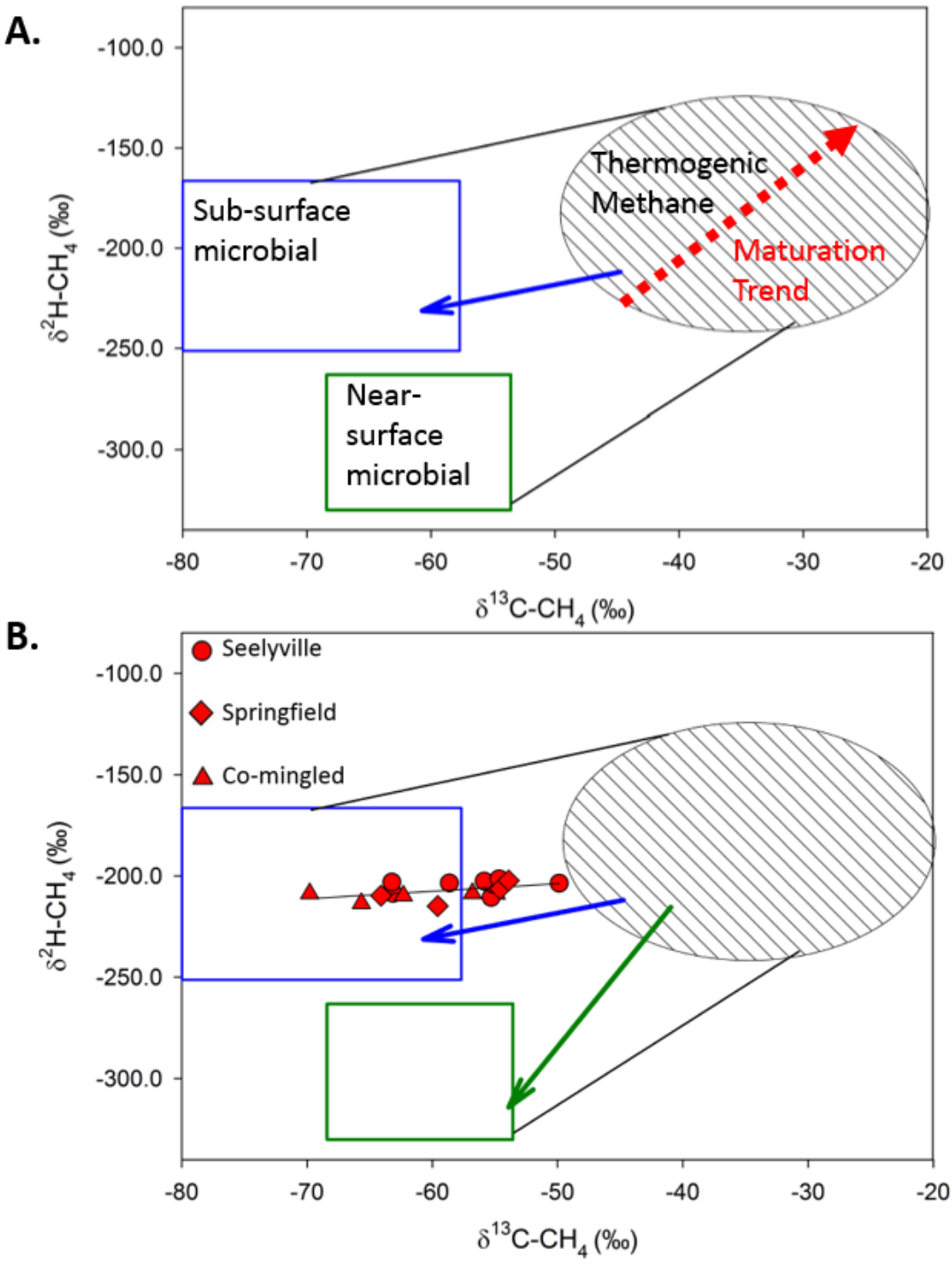


Figure 8: Plots of δ^2H-CH_4 vs. δ^{13}C-CH_4 with the top plot denoting sub-surface microbial, near surface microbial and thermogenic natural gas compositions (A) and the bottom plot displaying data from producing CBM wells sampled in this study (B).

Tables

Table 1: Hydrocarbon and major gas composition

SampleID	CoalGasProductionUnit	WellMaxdepthScreened(m.)	CH4	C2H6	C3H8	C4H10 n	C4H10 i	C5H12 n	C5H12 i	N2	CO2	Inert Gases CO_2+ N_2
			ccSTP/cc	ccSTP/cc	ccSTP/cc	ccSTP/cc	ccSTP/cc	ccSTP/cc	ccSTP/cc	ccSTP/cc	ccSTP/cc	ccSTP/cc
		76										
CreedMine*	Springfield		0.922	$1.27x10^{-4}$	$<1x10^{-5}$	$<1x10^{-5}$	$<1x10^{-5}$	$<1x10^{-5}$	$<1x10^{-5}$	0.066	0.012	0.078
Stultz	Springfield	72	0.961	$2.05x10^{-4}$	$<1x10^{-5}$	$<1x10^{-5}$	$<1x10^{-5}$	$<1x10^{-5}$	$<1x10^{-5}$	0.031	0.008	0.039
Mayfield-1	Springfield	91	0.965	$4.50x10^{-4}$	$<1x10^{-5}$	$<1x10^{-5}$	$<1x10^{-5}$	$<1x10^{-5}$	$<1x10^{-5}$	0.023	0.013	0.036
Alexander-1	Springfield	107	0.953	$5.07x10^{-4}$	$<1x10^{-5}$	$<1x10^{-5}$	$<1x10^{-5}$	$<1x10^{-5}$	$<1x10^{-5}$	0.043	0.004	0.047
Creed-2	Springfield	76	0.950	$1.73x10^{-4}$	$<1x10^{-5}$	$<1x10^{-5}$	$<1x10^{-5}$	$<1x10^{-5}$	$<1x10^{-5}$	0.044	0.006	0.05
Bolenbaugh	Seelyville	173	0.939	$4.85x10^{-4}$	$<1x10^{-5}$	$<1x10^{-5}$	$<1x10^{-5}$	$<1x10^{-5}$	$<1x10^{-5}$	0.048	0.008	0.056
T.Cole	Seelyville	177	0.959	$5.04x10^{-4}$	$<1x10^{-5}$	$<1x10^{-5}$	$<1x10^{-5}$	$<1x10^{-5}$	$<1x10^{-5}$	0.034	0.007	0.041
Alexander-2	Seelyville	213	0.943	$4.38x10^{-4}$	$<1x10^{-5}$	$<1x10^{-5}$	$<1x10^{-5}$	$<1x10^{-5}$	$<1x10^{-5}$	0.043	0.008	0.051
Vic	Seelyville	171	0.963	$3.73x10^{-4}$	$<1x10^{-5}$	$<1x10^{-5}$	$<1x10^{-5}$	$<1x10^{-5}$	$<1x10^{-5}$	0.021	0.017	0.038
Doherty-1	Seelyville	176	0.959	$2.47x10^{-4}$	$<1x10^{-5}$	$<1x10^{-5}$	$<1x10^{-5}$	$<1x10^{-5}$	$<1x10^{-5}$	0.032	0.010	0.042
Arnett-1	Seelyville	153	0.961	$3.82x10^{-4}$	$<1x10^{-5}$	$<1x10^{-5}$	$<1x10^{-5}$	$<1x10^{-5}$	$<1x10^{-5}$	0.030	0.009	0.039
Arnett-3	Seelyville	167	0.954	$2.38x10^{-4}$	$<1x10^{-5}$	$<1x10^{-5}$	$<1x10^{-5}$	$<1x10^{-5}$	$<1x10^{-5}$	0.040	0.005	0.045
McCain	Seelyville	175	0.899	$9.25x10^{-5}$	$<1x10^{-5}$	$<1x10^{-5}$	$<1x10^{-5}$	$<1x10^{-5}$	$<1x10^{-5}$	0.085	0.006	0.091
Wheeler	Seelyville	175	0.942	$1.09x10^{-3}$	$<1x10^{-5}$	$<1x10^{-5}$	$<1x10^{-5}$	$<1x10^{-5}$	$<1x10^{-5}$	0.041	0.007	0.048
Hancock-1	Co-mingled	158	0.948	$7.15x10^{-5}$	$<1x10^{-5}$	$<1x10^{-5}$	$<1x10^{-5}$	$<1x10^{-5}$	$<1x10^{-5}$	0.049	0.004	0.053
Coulson-1	Co-mingled	174	0.973	$4.73x10^{-4}$	$<1x10^{-5}$	$<1x10^{-5}$	$<1x10^{-5}$	$<1x10^{-5}$	$<1x10^{-5}$	0.021	0.006	0.027
F.Willis	Co-mingled	No-info	0.902	$4.25x10^{-4}$	$<1x10^{-5}$	$<1x10^{-5}$	$<1x10^{-5}$	$<1x10^{-5}$	$<1x10^{-5}$	0.075	0.010	0.085
Unger	Co-mingled	185	0.875	$7.84x10^{-5}$	$<1x10^{-5}$	$<1x10^{-5}$	$<1x10^{-5}$	$<1x10^{-5}$	$<1x10^{-5}$	0.097	0.009	0.106
E.Hobbs-1	Co-mingled	No-info	0.938	$3.12x10^{-4}$	$<1x10^{-5}$	$<1x10^{-5}$	$<1x10^{-5}$	$<1x10^{-5}$	$<1x10^{-5}$	0.052	0.011	0.063
Gimoson	Co-mingled	No-info	0.971	$5.40x10^{-4}$	$<1x10^{-5}$	$<1x10^{-5}$	$<1x10^{-5}$	$<1x10^{-5}$	$<1x10^{-5}$	0.020	0.009	0.029

Table 2: Statistical summary of hydrocarbon and major gas composition

All Samples	CH_4 ccSTP/cc	C_2H_6 ccSTP/cc	C_3H_8 ccSTP/cc	$C_4H_{10}n$ ccSTP/cc	$C_4H_{10}i$ ccSTP/cc	$C_5H_{12}n$ ccSTP/cc	$C_5H_{12}i$ ccSTP/cc	N_2 ccSTP/cc	CO_2 ccSTP/cc
Average	**0.944**	**$3.6x10^{-4}$**	**-**	**-**	**-**	**-**	**-**	**0.045**	**0.009**
Minimum	**0.875**	**$7.1x10^{-5}$**	**-**	**-**	**-**	**-**	**-**	**0.020**	**0.004**
Maximum	**0.973**	**$1.1x10^{-3}$**	**-**	**-**	**-**	**-**	**-**	**0.097**	**0.017**
St. Dev.	**0.026**	**$2.3x10^{-4}$**	**-**	**-**	**-**	**-**	**-**	**0.021**	**0.003**
Springfield									
Average	**0.950**	**$2.9x10^{-4}$**	**-**	**-**	**-**	**-**	**-**	**0.041**	**0.009**
Minimum	**0.922**	**$1.3x10^{-4}$**	**-**	**-**	**-**	**-**	**-**	**0.023**	**0.004**
Maximum	**0.965**	**$5.1x10^{-4}$**	**-**	**-**	**-**	**-**	**-**	**0.066**	**0.013**
St. Dev.	**0.017**	**$1.7x10^{-4}$**	**-**	**-**	**-**	**-**	**-**	**0.017**	**0.004**
Seelyville									
Average	**0.947**	**$4.3x10^{-4}$**	**-**	**-**	**-**	**-**	**-**	**0.041**	**0.009**
Minimum	**0.899**	**$9.2x10^{-5}$**	**-**	**-**	**-**	**-**	**-**	**0.021**	**0.005**
Maximum	**0.963**	**$1.1x10^{-3}$**	**-**	**-**	**-**	**-**	**-**	**0.085**	**0.017**
St. Dev.	**0.020**	**$2.8x10^{-4}$**	**-**	**-**	**-**	**-**	**-**	**0.018**	**0.003**
Co-mingled									
Average	**0.934**	**$3.2x10^{-4}$**	**-**	**-**	**-**	**-**	**-**	**0.052**	**0.008**
Minimum	**0.875**	**$7.1x10^{-5}$**	**-**	**-**	**-**	**-**	**-**	**0.020**	**0.004**
Maximum	**0.973**	**$5.4x10^{-4}$**	**-**	**-**	**-**	**-**	**-**	**0.097**	**0.011**
St. Dev.	**0.039**	**$2.0x10^{-4}$**	**-**	**-**	**-**	**-**	**-**	**0.030**	**0.003**

Table 3: Hydrocarbon isotopic and molecular composition.

Sample ID	Coal Gas Production Unit	Well Max depth Screened (m.)	$\delta^{13}C\text{-}CH_4$	$\delta^{2}H\text{-}CH_4$	$\frac{CH_4}{C_2H_6+}$
			per mil	per mil	
Creed Mine	Springfield	76	-64.10	-209.7	7,256.6
Stultz	Springfield	73	-58.10	n.r.	4,687.6
Mayfield-1	Springfield	91	-53.90	-202.3	2,145.6
Alexander-1	Springfield	107	-54.60	-206.4	1,879.6
Creed-2	Springfield	76	-59.58	-214.9	5,489.4
Bolenbaugh	Seelyville	173	-55.31	-210.6	1,935.1
T.Cole	Seelyville	177	-55.20	-203.9	1,901.1
Alexander-2	Seelyville	213	-63.14	-208.7	2,154.6
Vic	Seelyville	171	-55.87	-202.6	2,578.9
Doherty-1	Seelyville	176	-57.30	n.r.	3,879.6
Arnett-1	Seelyville	153	-54.68	-201.4	2,513.4
Arnett-3	Seelyville	167	-58.64	-203.5	4,002.1
McCain	Seelyville	175	-63.24	-203.1	9,725.6
Wheeler	Seelyville	175	-49.87	-203.6	867.6
Hancock-1	Co-mingled	158	-62.32	-209.8	13,256.6
Coulson-1	Co-mingled	174	-54.77	n.r.	2,057.9
F. Willis	Co-mingled	No-info	-65.67	-213.6	2,124.5
Unger	Co-mingled	185	-69.80	-208.7	11,164.4
E.Hobbs-1	Co-mingled	No-info	-56.80	-208.6	3,001.6
Gimoson	Co-mingled	No-info	-54.90	-208.9	1,796.6

Table 4: Statistical summary of hydrocarbon isotopic and molecular composition.

	$\delta^{13}C\text{-}CH_4$	$\delta^{2}H\text{-}CH_4$	$\frac{CH_4}{C_2H_6+}$
All Samples	**per mil**	**per mil**	
Average	**-58.39**	**-207.1**	**4348.5**
Minimum	**-69.80**	**-214.9**	**867.6**
Maximum	**-49.87**	**-201.4**	**13256.6**
St. Dev.	**4.89**	**4.1**	**3520.9**
Springfield			
Average	**-58.06**	**-208.3**	**3992.3**
Minimum	**-64.10**	**-214.9**	**1879.6**
Maximum	**-53.90**	**-202.3**	**7256.6**
St. Dev.	**4.13**	**5.3**	**2517.5**
Seelyville			
Average	**-57.03**	**-204.7**	**3797.8**
Minimum	**-63.24**	**-210.6**	**1901.1**
Maximum	**-49.87**	**-201.4**	**9725.6**
St. Dev.	**4.23**	**3.2**	**2523.7**
Co-mingled			
Average	**-60.71**	**-209.9**	**5412.1**
Minimum	**-69.80**	**-213.6**	**867.6**
Maximum	**-54.77**	**-208.6**	**13256.6**
St. Dev.	**6.23**	**2.1**	**5350.7**

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